

Electronic Supplementary Information

Sticking coefficient and pressure dependence of desorption rate in the Statistical Rate Theory approach to the kinetics of gas adsorption. Carbon monoxide adsorption/desorption rates on the polycrystalline rhodium surface

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1. *Development of the expressions for the chemical potentials of a two-component mixture on the energetically heterogeneous surface with full correlation of the adsorption energies of both components*

The full correlation of the adsorption energies means that these energies differ only by a constant. For isotopes this difference is negligibly small, so it may be assumed that $\varepsilon = \varepsilon_A = \varepsilon_B$. Then, the chemical potentials of these components on the energetically *uniform* surface can be expressed as follows,

$$\frac{\mu_A}{kT} = \ln \frac{\theta_A}{(1 - \theta_A - \theta_B) q e^{\varepsilon/kT}} \quad (1A)$$

$$\frac{\mu_B}{kT} = \ln \frac{\theta_B}{(1 - \theta_A - \theta_B) q e^{\varepsilon/kT}} \quad (2A)$$

After the following substitutions

$$\varepsilon_{cA} = -\mu_A - kT \ln q \quad (3A)$$

$$\varepsilon_{cB} = -\mu_B - kT \ln q \quad (4A)$$

equations (1A) and (2A) can be written in the following forms:

$$\theta_A = \frac{e^{\frac{\varepsilon - \varepsilon_{cA}}{kT}}}{1 + e^{\frac{\varepsilon - \varepsilon_{cA}}{kT}} + e^{\frac{\varepsilon - \varepsilon_{cB}}{kT}}} \quad (5A)$$

$$\theta_B = \frac{e^{\frac{\varepsilon - \varepsilon_{cB}}{kT}}}{1 + e^{\frac{\varepsilon - \varepsilon_{cA}}{kT}} + e^{\frac{\varepsilon - \varepsilon_{cB}}{kT}}} \quad (6A)$$

Let ε_x denote the following function:

$$\varepsilon_x = -kT \ln \left(e^{\frac{\varepsilon_{cA}}{kT}} + e^{\frac{\varepsilon_{cB}}{kT}} \right) \quad (7A)$$

Then, eqs. (5A) and (6A) can be transformed into the equivalent forms:

$$\theta_A = \frac{e^{\frac{-\varepsilon_{cA}}{kT}} e^{\frac{\varepsilon - \varepsilon_x}{kT}}}{e^{\frac{-\varepsilon_x}{kT}} 1 + e^{\frac{\varepsilon - \varepsilon_x}{kT}}} \quad (8A)$$

$$\theta_B = \frac{e^{\frac{-\varepsilon_{cB}}{kT}} e^{\frac{\varepsilon - \varepsilon_x}{kT}}}{e^{\frac{-\varepsilon_x}{kT}} 1 + e^{\frac{\varepsilon - \varepsilon_x}{kT}}} \quad (9A)$$

The above forms allow for application of integral equation and condensation approximation for averaging the local surface coverages over the existing energy domain of the heterogeneous surface. Let us note that the first terms on the r.h.s. of eqs. (8A) and (9A) are independent of ε , thus integration of these equations with a distribution function $\chi(\varepsilon)$ is exactly the same as in the case of Langmuir isotherm being the kernel of integral equation (31). For the DA distribution function (33), this integration leads to the following expressions describing the total surface coverages of components *A* and *B* (θ_{tA} and θ_{tB}) on the energetically heterogeneous surface:

$$\theta_{tA} = \frac{e^{\frac{-\varepsilon_{cA}}{kT}}}{e^{\frac{-\varepsilon_{cA}}{kT}} + e^{\frac{-\varepsilon_{cB}}{kT}}} \exp \left(- \left(- \frac{kT}{\delta} \ln \left(e^{\frac{\varepsilon_{cA}}{kT}} + e^{\frac{\varepsilon_{cB}}{kT}} \right) - \frac{\varepsilon_0}{\delta} \right)^r \right) \quad (10A)$$

$$\theta_{tB} = \frac{e^{\frac{-\varepsilon_{cB}}{kT}}}{e^{\frac{-\varepsilon_{cA}}{kT}} + e^{\frac{-\varepsilon_{cB}}{kT}}} \exp \left(- \left(- \frac{kT}{\delta} \ln \left(e^{\frac{\varepsilon_{cA}}{kT}} + e^{\frac{\varepsilon_{cB}}{kT}} \right) - \frac{\varepsilon_0}{\delta} \right)^r \right) \quad (11A)$$

Solving equations (10A) and (11A) with respect to ε_{cA} and ε_{cB} and using the substitutions (3A) and (4A) lead directly to the expressions for the chemical potentials of both components on the energetically heterogeneous surface:

$$\mu_A = -kT \ln \left[\frac{\theta_{tA} + \theta_{tB}}{\theta_{tA}} \exp \left(\frac{\delta}{kT} \left(\ln \frac{1}{\theta_{tA} + \theta_{tB}} \right)^{\frac{1}{r}} + \frac{\varepsilon_0}{kT} \right) \right] - kT \ln q \quad (12A)$$

$$\mu_B = -kT \ln \left[\frac{\theta_{tA} + \theta_{tB}}{\theta_{tB}} \exp \left(\frac{\delta}{kT} \left(\ln \frac{1}{\theta_{tA} + \theta_{tB}} \right)^{\frac{1}{r}} + \frac{\varepsilon_0}{kT} \right) \right] - kT \ln q \quad (13A)$$

2. *Equations describing the kinetics of adsorption of the two-component mixture of isotopes on the energetically heterogeneous surface*

To build up the set of equations describing the process of the kinetics of adsorption of the two-component mixture used by Yamada and Tamaru¹², let us note that this process was composed of two stages. The first was the adsorption of the single component *B*, the second, starting after the time t_1 , was the adsorption of the component *A* and desorption of the component *B*, both induced by the change of the composition of the gas phase (from the component *B* to *A*). The first stage is described by the following set of differential equations,

$$\left\{ \begin{array}{l} \frac{d\theta_{iA}}{dt} = 0 \\ \frac{d\theta_{iB}}{dt} = \frac{S_0 p_B}{N_0 \sqrt{2\pi m_B kT}} \left(1 - \theta_{iA}^{(e)}(p_A, p_B) - \theta_{iB}^{(e)}(p_A, p_B) \right) \left[K p_B e^{\frac{\mu_B(\theta_{iA}, \theta_{iB})}{kT}} - \frac{1}{K p_B} e^{\frac{\mu_B(\theta_{iA}, \theta_{iB})}{kT}} \right] \\ \frac{dp_A}{dt} = 0 \\ \frac{dp_B}{dt} = \frac{S_0 kT}{h \sqrt{2\pi m_B kT}} \left(\frac{p_0}{\sqrt{T_0}} - \frac{p_B}{\sqrt{T}} \right) - \frac{d\theta_{iB}}{dt} N_0 S_A \frac{kT}{S_G h} \end{array} \right. \quad (14A)$$

with the boundary conditions: $p_A(0)=p_0$; $p_B(0)=0$; $\theta_{iA}(0)=0$; $\theta_{iB}(0)=0$.

The functions $\theta_{iA}^{(e)}$ and $\theta_{iB}^{(e)}$ are the equilibrium adsorption isotherms, they can be directly derived from the appropriate chemical potentials, i.e. eqs.(12A, 13A) by equating them to the chemical potentials of these components in the gas phase. The process of adsorption of the component *B* is, of course, described by the *volume dominated* version of the SRT kinetic equation.

The solution of set (14A) lasts up to time t_1 . Then, the experimental conditions change and the process is continuing with the following set of equations,

$$\left\{ \begin{array}{l} \frac{d\theta_{iA}}{dt} = \frac{S_0 p_A}{N_0 \sqrt{2\pi m_A kT}} \left(1 - \theta_{iA}^{(e)}(p_A, p_B) - \theta_{iB}^{(e)}(p_A, p_B) \right) \left[K p_A e^{\frac{\mu_A(\theta_{iA}, \theta_{iB})}{kT}} - \frac{1}{K p_A} e^{\frac{\mu_A(\theta_{iA}, \theta_{iB})}{kT}} \right] \\ \frac{d\theta_{iB}}{dt} = \frac{S_0}{N_0 \sqrt{2\pi m_B kT}} p_B^{(e)}(\theta_{iA}, \theta_{iB}) (1 - \theta_A - \theta_B) \left[K p_B e^{\frac{\mu_B(\theta_{iA}, \theta_{iB})}{kT}} - \frac{1}{K p_B} e^{\frac{\mu_B(\theta_{iA}, \theta_{iB})}{kT}} \right] \\ \frac{dp_A}{dt} = \frac{S_0 kT}{h \sqrt{2\pi m_A kT}} \left(\frac{p_0}{\sqrt{T_0}} - \frac{p_A + \alpha p_B}{\sqrt{T}} \right) - \frac{d\theta_{iA}}{dt} N_0 S_A \frac{kT}{S_G h} \\ \frac{dp_B}{dt} = \frac{S_0 kT}{h \sqrt{2\pi m_B kT}} \left(\frac{\alpha p_B}{\sqrt{T}} - \frac{p_B}{\sqrt{T}} \right) - \frac{d\theta_{iB}}{dt} N_0 S_A \frac{kT}{S_G h} \end{array} \right. \quad (15A)$$

And the following boundary conditions must be applied: $p_A(t_1)=0$; $p_B(t_1)=p_B(t_1)$; $\theta_A(t_1)=0$; $\theta_B(t_1)=\theta_B(t_1)$.

The process of adsorption of the component A is described by the *volume dominated* version of the SRT equation, as in the case of adsorption of the component B in the previous set (14A). However, the desorption of the component B must now be described by the *solid dominated* version of the SRT equation since after the time t_1 the gas phase is evacuated from the component B and thus the conditions typical of the *solid dominated* version appear. The function $p_B^{(e)}$ can be derived from the equilibrium isotherm equations.

Some explanations require the equations describing the partial pressures evolution in set (15A). They differ from the equation in set (14A) where the single component process takes place. The terms αp_B which appear in the (15A) come from some simplification concerning the composition of the bulk gas phase being under the pressure p_0 . The desorption of the component B makes the bulk gas phase a two-component mixture (A,B). Unfortunately, the temporal quantitative composition of that mixture is unknown. Therefore the following assumption was made. The bulk gas phase is kept under the constant pressure p_0 , thus some part of B molecules coming from desorption removes from the bulk the same part of A molecules, thus the flux of A molecules to the near-surface region is lowered by $\alpha p_B / \sqrt{2\pi m_A kT}$, ($m_A \approx m_B$), where α is an adjustable parameter. Simultaneously, the same part of B molecules acts as the source of B molecules which can enter again the near-surface region. Of course, such treatment is only simplification; however, it appeared as a very good approximation since set (15A) describes the experimental data very well using the same values of parameters as those estimated from the single component model described in the article. The parameter α was estimated to be equal to 0.5.

The results obtained using set (15A) are shown in Figures 10 and 11 in the article.